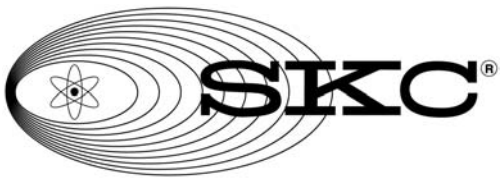
Validation of Propyl Bromide Using SKC Passive Samplers 575-001 and 575-002



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Propyl Bromide

VALIDATION OF TWO DIFFUSIVE SAMPLERS (SKC Inc., 575-001 and 575-002) for PROPYL BROMIDE

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ABSTRACT

At the request of Albemarle Corporation (Baton Rouge, LA), a validation was performed on the ability of the SKC 575-001 and 575-002 diffusive samplers to accurately sample propyl bromide in workplace air. A desorption efficiency (DE) study involved samplers spiked at 0.05, 0.1, 0.5, 1, and 2 times the Albemarle in-house exposure limit (100 ppm) for an 8-hour period. The uptake rate was determined for samplers exposed to 100 ppm and 200 ppm propyl bromide for various exposures time periods. To determine the effects of low concentration on uptake a set of samplers were exposed to 10 ppm propyl bromide. Exposure to various time periods at 10% RH and 80% RH at 25 C was used to determine the effect of humidity on uptake. A study also was conducted on the uptake rate at 40 C to confirm the ability of the samplers to be used at higher temperatures and humidities. A storage study at both room and freezer temperatures was also performed. Based on the combined results of 52 samplers exposed and analyzed within 24 hours, the mean uptake rate was 14.4 ml/min (CV=5.6%) for the 575-001 badges and 14.7 ml/min (CV=2.1%) for the 575-002 badges, over a relative humidity of 10 to 80% and at temperatures from 25 to 40 C. Both sampling rates were within 10% of the calculated rate of 15.8 ml/min. Both sets of samplers showed good stability for up to four weeks when stored in a freezer.

INTRODUCTION

Propyl bromide (1-bromopropane, CAS # 106-94-5) has many uses such as pharmaceutical intermediates, organic synthesis, and as a solvent. The Albemarle Corporation has a set OEL of 100 ppm. Vapor is irritating to the eyes, mucous membranes, and upper respiratory tract. Propyl bromide affects the central nervous system at high concentration, however, the chemical, physical, and toxicological properties have not been thoroughly investigated.

The validation of diffusive samplers is important for many reasons [(1)]. One reason is that a diffusive sampler does not always have a backup section to ensure that all the hazardous compound has been collected. In addition backup sections that are provided with some samplers do not provide assured

accuracy in all cases [2]. Secondly, like sample tubes, the sorbent media of a diffusive sampler is exposed to the varying conditions of the environment. Factors that can affect complete sample uptake rate and retention include: temperature, humidity, chemical hazard concentration, time of exposure, reverse diffusion from sorbent surface, interfering chemicals, sampler orientation, wind velocity and atmospheric pressure.

SKC has followed in previous studies the National Institute for Occupational Safety and Health (NIOSH) protocol for the validation of diffusive samplers [3,4]. This method of validation assures that the samplers will provide an accurate measure of worker exposure. However, only SKC has made extensive use of this protocol, and recently, NIOSH has supported the development of a new ASTM Standard Practice [5]. In addition, ANSI has published a new Standard Guide [6]. The ANSI Guide describes tests to determine the effects of the factors listed above, without stipulating a required range of conditions. The experiments described in this publication were based on the ANSI Guide. The ASTM Standard is similar and allows for flexibility in the experimental procedure. The effects of wind velocity and sampler orientation to the wind are device specific and only need to be evaluated for a single chemical [7]. The SKC 575 Series samplers have been tested to show no significant effects over the range 10 to 150 cm sec^{-1} wind velocity at parallel or perpendicular orientation [7]. A recent study in the U.K. has shown typical workplace air velocities to be distributed around a mean of 30 to 40 cm sec^{-1} [8]. The effect of pressure has been found to follow expected relationships. All other validation factors were tested in this study so that it may be considered a full validation of 575 Series samplers for propyl bromide.

EXPERIMENTAL

Reagents and Apparatus

Propyl bromide (Aldrich Chemical Co., Inc., Milwaukee, WI, U.S.A.) was separated on a 6-foot, 20% SP-2100 on 80/100 mesh Supelcoport® packed column (Supelco, Inc., Supelco Park, Bellefonte, PA, U.S.A.). The GC was a Mikrolab, iso-thermal, with a flame ionization detector. The diffusive (passive) samplers used were SKC 575-001 samplers containing coconut charcoal and SKC 575-002 samplers containing Anasorb® 747[9]. Standard atmospheres around the Albemarle Corporation

in-house limit value (100 ppm, 25 C, 80% RH) were generated using an atmosphere chamber. The atmosphere was calibrated using a combination of calculations, 1-ml gas injections, and Anasorb 747 charcoal tubes (Cat. No. 226-81A, SKC Inc., Eighty Four, PA, U.S.A.). Carbon disulfide (Aldrich Chemical Co., Inc., Milwaukee, WI, U.S.A.) was used as the desorbing solution; isooctane (Fisher Scientific, Fair Lawn, NJ, U.S.A.) was used for an internal standard. The detection limit for propyl bromide was determined on the basis of repeated observation of lowest measurable concentration of 15 μg/2 ml. The amount was repeatedly recovered with high precision (6.3%) and corresponds to a concentration level of 6.4 ppm.

PROCEDURES

The analytical recovery (desorption efficiency) was determined by using four samplers at each exposure level to be tested. The loading was based on equivalent 8-hour exposures to 0.05, 0.1, 0.5, 1.0 and 2 times the Albemarle in-house limit value (100 ppm). A 10 μl volume of a carbon disulfide solution which contained the amount of the analyte expected from the given exposure level based on the calculated uptake rate (15.8 ml/min) was injected directly through the rear ports of the samplers. The samplers were capped and stored at room temperature overnight to equilibrate, and were desorbed the following day. The samplers were desorbed by the introduction of 2 ml of carbon disulfide into the body of the sampler, followed by shaking for 30 min on a specially designed desorption shaker (Cat. No. 226d –03, SKC Inc., Eighty Four, PA, U.S.A.). The amount recovered on analysis was determined as a percentage of the initial loading. To determine if moisture would effect the desorption efficiency, a set of samplers were exposed to 80% RH before the samplers were spiked as outlined above. A similar study was performed for the Anasorb 747 sample tubes.

The calculated uptake rate of the samplers for propyl bromide was verified for periods of 0.5, 2, 4, 6, and 8-hour exposures to a constant atmosphere of twice the Albemarle in-house exposure limit at 80% relative humidity levels (25 C) and 0.5, 2, and 8-hour exposures to the same concentration at 10% relative humidity. Four samplers were exposed simultaneously to the atmosphere for each time period. After exposure, the samplers were capped and analyzed the following day. A further set of 24 samplers were exposed to 100 ppm under conditions of 25 C and 80% RH for 4 hours, and these were used for the storage study (12 samplers for each storage study – room temp and -8 C). After these

samplers were removed from the chamber, three were analyzed that day and the others were capped and kept at room temperature or -8 C for up to four weeks. Sets of three samplers were analyzed each week with the exception of the third week in which none of the samplers were tested. Sets of four samplers were also exposed to 10 ppm for 0.5, 4, and 8-hour time periods to show the effects of low concentration on the uptake rate. In addition, sets of four samplers were exposed for four hours to an atmosphere of 100 ppm at 40 C and 80% RH to determine if the higher temperature would have any effect on the uptake rate.

One-ml gas injections were taken at intervals during the exposure periods to give real-time estimates of fluctuations in the atmosphere concentration. The mean of the 1-ml injections (15 to 20 injections) was used as a check on the atmosphere calibration. In addition, sorbent tubes (Anasorb 747, Cat. No. 226-81A, SKC Inc., Eighty Four, PA, U.S.A.) were used to determine the concentration. Samples were taken at 50 ml/min for 2 hours each to ensure the concentration of the atmospheric chamber matched the theoretical value expected. The results obtained from the 1-ml injections and the sorbent tubes were within 10% of the calculated value. Therefore, the calculated value was used as the true concentration, which is in line with most protocol recommendations.

RESULTS and DISCUSSION

The desorption efficiency results for propyl bromide are given in Table 1 for both the diffusive samplers and the sorbent tubes. The results for the study performed using samplers exposure to 80% RH (8 hours for the diffusive samplers and 2 hours at 50 ml/min for the sorbent tubes) were similar to the results for dry sorbents, therefore, the dry desorption efficiency was used for all the calculations. The mean recovery for propyl bromide on the SKC 575-001 badges was 100% (1.9% RSD), 107% (3.8% RSD) for the SKC 575-002 samplers, and 100% (1.2% RSD) for the SKC 226-81A sorbent tubes. The propyl bromide results were consistent even at the low levels of concentration

The results for the uptake rate studies and how they compare to the rate calculated at standard temperature and pressure are given in Table 2. The mean uptake rate for propyl bromide was calculated to be 14.3 ml/min for the SKC 575-001 samplers and 14.7 ml/min for the SKC 575-002 samplers. These results for the uptake rate are within 10% of the rate calculated (15.8 ml/min). A combined rate of 14.5 ml/min is recommended for use with either sampler. A factorial analysis of variance indicated a significant difference

between the results obtained at 10 ppm from those obtained at 100 or 200 ppm. This difference was observed again when the experiment was repeated. However, the difference is opposite to that which might be expected from overloading at high concentrations. If the phenomenon is real, then use of the 14.5 ml/min mean uptake rate will slightly underestimate (<10%) low concentrations. There is no effect of sampling time or humidity

The uptake rate of both samplers (SKC 575-001 and 575-002) at 40 C and 80% relative humidity were within 10% of the expected (16.2 ml/min) uptake rate (Table 3).

The storage stability results show that there was less than 10% change between the initial week and the fourth week period in the freezer and at room temperature for both the 575-001 and the 575-002 samplers.

CONCLUSION

The diffusive samplers 575-001 and 575-002 have been validated for sampling propyl bromide for occupational hygiene situations according to SKC's modifications to the NIOSH protocol. The validation method used is equivalent to Level 1A evaluation of EN 838[10] and meets the requirements of recent ASTM and ANSI standards. Propyl bromide can be sampled accurately with the SKC diffusive samplers 575-001 and 575-002 at an experimentally determined uptake rate of 14.4 ml/min (CV 5.6%) and 14.7 ml/min (2.1%) respectively. Using a mean value of 14.5 ml/min for either sampler would not introduce significant bias. The data obtained through this study shows the samplers can be used at concentrations up to twice the Albemarle in-house exposure limit (100 ppm) and at high temperatures and humidity. A desorption efficiency correction of 100% is applied for the 575-001 samplers and 107% for the 575-002 samplers. The Anasorb 747 sorbent tubes have a desorption efficiency correction of 100%. Both 575-001 and 575-002 samplers show at least a 90% recovery when stored for up to four weeks (at room temperature or -8 C).

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Table 1. Desorption Efficiency (%)

Sampler	0.05 x PEL	0.1 x PEL	0.5 x PEL	1 x PEL	2 x PEL	Average
575-001	99.5	99.5	102.7	99.8	100.5	100
575-002	104.7	106.9	107.3	106.4	110.7	107
226-81A	99.2	102.8	99.8	100.6	99.6	100

Table 2. Sampling Rate and Capacity for Propyl Bromide

200 ppm Propyl Bromide (25 C and 80% RH)				
	575-001 Samplers		575-002 Samplers	
Time (hr)	Micrograms	Sampling Rate (ml/min)	Micrograms	Sampling Rate (ml/min)
0.5	475	15.7	420	14.0
	475	15.7	421	14.0
	450	14.9	453	15.0
	450	14.9	453	15.0
2	1750	14.5	1738	14.1
	1765	14.6	1682	13.9
	1760	14.6	1776	14.7
	1910	15.8	1645	13.6
4	3625	15.0	3561	14.8
	3685	15.3	3561	14.8
	3525	14.6	3827	15.9
	3375	14.0	3841	15.9
6	4940	13.6	5794	16.0
	5000	13.8	5958	16.5
	5150	14.2	6075	16.8
	4750	13.1	5607	15.5
8	6690	13.9	7121	14.8
	6110	12.7	7406	15.3
	6475	13.4	8154	16.9
	6800	14.1	7514	15.6
200 ppm Propyl Bromide (25 C and 10% RH)				
Time (hr)	Micrograms	Sampling Rate (ml/min)	Micrograms	Sampling Rate (ml/min)
0.5	545	18.1	560	18.6
	590	19.6	514	17.0
	501	19.6	514	17.0
	505	19.7	560	18.6
2	1750	14.5	1636	13.6
	1725	14.3	1729	14.3
	1725	14.3	1551	12.9
	1660	13.8	1636	13.6
8	6000	12.4	6402	13.3
	6040	12.5	6878	14.2
	5650	11.7	6542	13.6
	6350	13.2	6262	13.0
100 ppm Propyl Bromide (25 C and 80% RH)				
Time (hr)	Micrograms	Sampling Rate (ml/min)	Micrograms	Sampling Rate (ml/min)
4	1775	14.7	1694	14.0
	1750	14.5	1694	14.0
	1750	14.5	1694	14.0
	1775	14.7	1729	14.3

Table 2. Sampling Rate and Capacity for Propyl Bromide (cont'd)

10 ppm Propyl Bromide (25 C and 80% RH)				
	575-001 Samplers		575-002 Samplers	
Time (hr)	Micrograms	Sampling Rate (ml/min)	Micrograms	Sampling Rate (ml/min)
0.5	17	11.7	23.4	16.2
	17	11.7	23.4	16.2
	21	14.5	24.3	16.8
4	160	13.8	20.0	13.8
	160	13.8	157	13.6
	165	14.2	154	13.3
	142	12.2	157	13.6
8	317	13.6	159	13.7
	293	12.6	257	11.0
	298	12.8	292	12.7
	322	13.8	320	13.8
			296	12.8
Mean Sampling Rate: 14.4 ml/min			Mean Sampling Rate: 14.7 ml/min	

Table 3. Sampling Rate at 40 C for Propyl Bromide

100 ppm Propyl Bromide (40 C and 80% RH)				
	575-001 Samplers		575-002 Samplers	
Time (hr)	Micrograms	Sampling Rate (ml/min)	Micrograms	Sampling Rate (ml/min)
4	2050	16.9	2327	19.1
	2015	16.6	2056	16.9
	2015	16.6	2033	16.7
	2000	16.5	2033	16.7
		Mean Rate: 16.6		Mean Rate: 17.4

Table 4. Storage Study for Propyl Bromide

	575-001 Samplers		575-002 Samplers	
Week	Room Temp. (25 C) Recovery (%)	Freezer (-8 C) Recovery	Room Temp. (25 C) Recovery (%)	Freezer (-8 C) Recovery
1	91.8	96.0	94.8	103.0
2	83.7	98.7	93.2	95.9
4	90.6	92.6	92.4	95.4